chloride are given in Table II. The values of entropy and free energy do not include the effects of nuclear spin or isotopes.

Through the coöperation of Dr. K. K. Kelley of the Pacific Experiment Station of the U. S. Bureau of Mines, a sample of the nickelous chloride prepared in this research was measured between 298 and 1336°K. The results have been published by Coughlin[15] who gives tables of the increments of the thermodynamic properties above 298.16°K.

To extend the present results to the higher temperatures

$$S^\circ_T = 23.33 + (S^\circ_T - S^\circ_{298.16})_{\text{Coughlin}}$$

$$\frac{H^\circ_T - H^0_0}{T} = \frac{11.531 \times 298.16 + (H^\circ_T - H^\circ_{298.16})_{\text{Coughlin}}}{T}$$

$$\frac{F^\circ_T - H^0_0}{T} = \frac{H^\circ_T - H^0_0}{T} - S^\circ_T$$

We thank Dr. J. E. Kunzler for assistance with the heat capacity measurements.

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[15] J. P. Coughlin, THIS JOURNAL, **73**, 5314 (1951).

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heats of Formation of Manganous Metasilicate (Rhodonite) and Ferrous Orthosilicate (Fayalite)

BY E. G. KING

RECEIVED FEBRUARY 23, 1952

The heats of formation of manganous metasilicate and ferrous orthosilicate were obtained by hydrofluoric acid solution calorimetry. The results are, respectively, $\Delta H_{298.16} = -308.22 \pm 0.34$ and $\Delta H_{298.16} = -346.0 \pm 1.1$ kcal./mole (heats of formation from the elements); and $\Delta H_{298.16} = -5.92 \pm 0.17$ and $\Delta H_{298.16} = -8.2 \pm 1.1$ kcal./mole (heats of formation from the oxides).

Recent papers[1,2] from this Laboratory reported heat of formation values at 298.16°K. for silicates of calcium, magnesium and zinc. The present paper gives the results of similar investigations of manganous metasilicate (rhodonite) and ferrous orthosilicate (fayalite).

Method and Materials.—The hydrofluoric acid solution calorimeter and method of operation were described previously.[1,2]

Reagent-grade hydrofluoric acid, 20.1% by weight, was used as the solution medium. The calorimeter was operated at 73.7° for the manganous silicate measurements and at 60.0° for ferrous silicate measurements.

All samples were dropped from 25° into the calorimeter at operating temperature. The samples were enclosed in gelatin capsules, for which corrections were determined by separate experiments. In each determination, 940.1 g. of the acid was employed. The masses of all other materials conformed stoichiometrically with 0.7420 g. of quartz.

The time required to reach thermal equilibrium ranged from 10 to 30 min., depending upon the substance being dissolved. Likewise, the calorimeter temperature rises ranged from 0.15 to 0.65°.

The calorimeter was calibrated several times during the course of each set of measurements, by supplying a measured amount of electrical energy and accurately determining the corresponding temperature rise.

Preparations and analyses of the manganous metasilicate (rhodonite) and ferrous orthosilicate (fayalite) used in this work were described by Kelley.[3]

Anhydrous ferrous chloride was prepared by the method of Kelley and Moore,[4] except that a hydrochloric acid solution of pure electrolytic iron (99.96%) was used as a starting material instead of ferrous chloride tetrahydrate. Analysis of the product gave 44.15% iron and 55.91% chlorine, as compared with the theoretical 44.06 and 55.94%.

The quartz was the same as that employed in previous work.[1,2] It was finely ground, water elutriated, and dried at 180°. Correction in the measurements was made for 0.4% residual moisture content.

Manganous oxide was prepared from the pure dioxide described by Kelley and Moore[5] by hydrogen reduction at 1100°. Analysis gave a purity of 99.92%.

The hydrochloric acid solution, which enters into the ferrous silicate measurements, was standardized against sodium carbonate prepared from reagent grade sodium bicarbonate. It analyzed 25.85% hydrogen chloride, corresponding to $HCl \cdot 5.806H_2O$.

Measurements and Results.—All thermal values are expressed in defined calories (1 cal. = 4.1833 int. joules). All weights were reduced to vacuum, and all molecular weights accord with the 1949 International Atomic Weights.

Table I presents schematically the process used in obtaining the heat of formation of manganous metasilicate.

TABLE I

HEAT OF FORMATION OF $MnSiO_3$(RHODONITE)(CAL./MOLE)

Reaction	ΔH	Uncertainty
(1) $MnSiO_3$ (c, 25°) + $8H^+$ (sol., 73.7°) + $6F^-$ (sol., 73.7°) → Mn^{++} (sol., 73.7°) + H_2SiF_6 (sol., 73.7°) + $3H_2O$ (sol., 73.7°)	−56,300	80
(2) SiO_2 (c, 25°) + $6H^+$ (sol., 73.7°) + $6F^-$ (sol., 73.7°) → H_2SiF_6 (sol., 73.7°) + $2H_2O$ (sol., 73.7°)	−33,290	80
(3) MnO (c, 25°) + $2H^+$ (sol., 73.7°) → Mn^{++} (sol., 73.7°) + H_2O (sol., 73.7°)	−28,930	130
(4) MnO (c, 25°) + SiO_2 (c, 25°) → $MnSiO_3$ (c, 25°)	− 5,920	170

$$\Delta H_4 = \Delta H_1 + \Delta H_3 - \Delta H_1$$

Six determinations of the heat of reaction (1) were made, the results being −56,250, −56,450, −56,180, −56,260, −56,290 and −56,390 cal. The mean value is −56,300 ± 80 cal.

The heat of reaction (2) was measured in an earlier research,[2] under identical conditions, as −33,290 ± 80 cal.

Reaction (3) was conducted after first dissolving the amount of quartz required by reaction (2).

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[1] D. R. Torgeson and Th. G. Sahama, THIS JOURNAL, **70**, 2156 (1948).

[2] E. G. King, *ibid.*, **73**, 656 (1951).

[3] K. K. Kelley, *ibid.*, **63**, 2750 (1941).

[4] K. K. Kelley and G. E. Moore, *ibid.*, **65**, 1264 (1943).

[5] K. K. Kelley and G. E. Moore, *ibid.*, **65**, 782 (1943).

This makes the composition of the final solution, after conducting reactions (2) and (3) consecutively, identical with the final solution after reaction (1). Nine measurements of the heat of reaction (3) gave −29,200, −28,650, −28,760, −28,830, −29,060, −29,140, −28,850, −29,080 and −28,770 cal. The mean value is −28,930 ± 130 cal.

The heat of formation of manganous metasilicate from quartz and crystalline manganous oxide at 298.16°K. is obtained from $\Delta H_2 + \Delta H_3 - \Delta H_1$ as − 5,920 ± 170 cal./mole. The heat of formation from the elements is obtained by combining this value with Southard and Shomate's[6] result for the heat of formation of manganous oxide (−92,040 ± 110 cal./mole) and the heat of formation of quartz[7] (−210,260 ± 270 cal./mole). The result is $\Delta H_{298\cdot16} = -308{,}220 \pm 340$ cal./mole.

The process for obtaining the heat of formation of ferrous orthosilicate is shown in Table II.

TABLE II

HEAT OF FORMATION OF Fe_2SiO_4(FAYALITE)(CAL./MOLE)

Reaction	ΔH	Uncertainty
(5) Fe_2SiO_4 (c, 25°) + $10H^+$ (sol., 60°) + $6F^-$ (sol., 60°) → H_2SiF_6 (sol., 60°) + $2Fe^{++}$ (sol., 60°) + $4H_2O$ (sol., 60°)	− 80,580	120
(6) SiO_2 (c, 25°) + $6H^+$ (sol., 60°) + $6F^-$ (sol., 60°) → H_2SiF_6 (sol., 60°) + $2H_2O$ (sol., 60°)	− 33,070	100
(7) $2FeCl_2$ (c, 25°) → $2Fe^{++}$ (sol., 60°) + $4Cl^-$ (sol., 60°)	− 35,950	160
(8) $4(HCl\cdot5.806\ H_2O)$ (l, 25°) → 23.22 H_2O (sol., 60°) + $4H^+$ (sol., 60°) + $4Cl^-$ (sol., 60°)	12,380	80
(9) 25.22 H_2O (l, 25°) → 25.22 H_2O (sol., 60°)	14,500	130
(10) $2FeCl_2$ (c, 25°) + SiO_2 (c, 25°) + 25.22 H_2O (l, 25°) → Fe_2SiO_4 (c, 25°) + $4(HCl\cdot5.806\ H_2O)$ (l, 25°)	13,680	270
$\Delta H_{10} = -\Delta H_5 + \Delta H_6 + \Delta H_7 - \Delta H_8 + \Delta H_9$		
(11) 2Fe (c, 25°) + $2Cl_2$ (g, 25°) → $2FeCl_2$ (c, 25°)	−163,800	1000
(12) $2H_2$ (g, 25°) + $2Cl_2$ (g, 25°) + 23.22 H_2O (l, 25°) → $4(HCl\cdot5.806\ H_2O)$ (l, 25°)	−150,960	200
(13) $2H_2$ (g, 25°) + O_2 (g, 25°) → $2H_2O$ (l, 25°)	−136,630	20
(14) Si (c, 25°) + O_2 (g, 25°) → SiO_2 (c, 25°)	−210,260	270
(15) 2Fe (c, 25°) + Si (c, 25°) + $2O_2$ (c, 25°) → Fe_2SiO_4 (c, 25°)	−346,050	1090
$\Delta H_{15} = \Delta H_{10} + \Delta H_{11} - \Delta H_{12} + \Delta H_{13} + \Delta H_{14}$		

It should be noted that the final solution obtained after reactions (5) and (8) are conducted consecutively is identical with the final solution obtained after conducting reactions (6), (7) and (9) consecutively.

Eight measurements of the heat of reaction (5) gave −80,640, −80,680, −80,450, −80,770, −80,480, −80,800, −80,380 and −80,460 cal. The mean value is −80,580 ± 120 cal.

Seven determinations of the heat of reaction (6) were made. The results are −33,020, −33,030, −32,960, −32,910 −33,260, −33,240 and −33,070 cal., the mean being −33,070 ± 100 cal.

Six determinations of the heat of reaction (7) gave −35,840, −35,880, −36,220, −36,160, −35,820 and −35,760 cal. The mean value is −35,950 ± 160 cal.

Nine measurements of the heat of reaction (8) gave 12,310, 12,280, 12,390, 12,300, 12,580, 12,320, 12,570, 12,300 and 12,380 cal. The mean value is 12,380 ± 80 cal.

Reaction (9), which is merely dilution by water of the calorimeter contents after reactions (6) and (7) are conducted consecutively, was studied (for purposes beyond the scope of this paper) at calorimeter temperatures between 50 and 73.7°. The measured heats are well-represented as a linear function of the calorimeter temperature. This function yields 14,500 ± 130 as the heat of reaction (9) under the conditions of Table II.

Reaction (10) represents the over-all process actually measured in the present work. The heat is obtained from the summation, $-\Delta H_5 + \Delta H_6 + \Delta H_7 - \Delta H_8 + \Delta H_9$, as $\Delta H_{298.16} = 13{,}680 \pm 270$ cal. This heat is combined with literature data to obtain the heat of formation of fayalite from the elements. The heat of reaction (11) is from Bichowsky and Rossini,[8] those of reactions (12) and (13) are from the N.B.S. Tables,[9] and that of reaction (14) is from Humphrey and King.[7] The final result for the summation, $\Delta H_{10} + \Delta H_{11} - \Delta H_{12} + \Delta H_{13} + \Delta H_{14}$, is $\Delta H_{298.16} = -346{,}050 \pm 1{,}090$ cal./mole, or in round numbers $\Delta H_{298.16} = -346{,}000 \pm 1{,}100$, for the heat of formation from the elements. This value suffers in accuracy principally from the uncertainty in the heat of reaction (11), and it may be improved whenever a better value of the heat of formation of ferrous chloride becomes available.

The non-existence of stoichiometric ferrous oxide as a thermodynamically stable, crystalline single phase precludes deriving an actual heat of formation of fayalite from the oxides; but the heat of an analogous reaction involving oxide of composition $Fe_{0.947}O$ may be obtained. Darken and Gurry[10] gave $\Delta H_{1523} = -63{,}080$ as the heat of formation of $Fe_{0.947}O$ from the elements. This value may be converted to 298.16°K. by means of the heat content data of Coughlin, King and Bonnickson[11] and Kelley.[12] The result is $\Delta H_{298.16} = -63{,}800 \pm 200$ cal./mole. Combination of the latter figure with the heat of formation of quartz[7] and the heat of reaction (15) leads to $\Delta H_{298.16} = -8{,}200 \pm 1{,}100$ cal. for the reaction

$$2Fe_{0.947}O(c) + 0.106\ Fe(c) + SiO_2(c) = Fe_2SiO_4(c)$$

By analogy this value may be designated as the "heat of formation from the oxides."

TABLE III

HEATS, ENTROPIES AND FREE ENERGIES OF FORMATION

Substance	$\Delta H_{298.16}$, kcal./mole	$\Delta S_{298.16}$, cal./deg./mole	$\Delta F°_{298.16}$, kcal./mole
	From the elements		
$MnSiO_3$	−308.22 ± 0.34	−64.3 ± 0.3	−289.05 ± 0.35
Fe_2SiO_4	−346.0 ± 1.1	−80.8 ± 0.5	−322.0 ± 1.1
	From the oxides		
$MnSiO_3$	−5.92 ± 0.17	−3.0 ± 0.3	−5.03 ± 0.19
Fe_2SiO_4	−8.2 ± 1.1	−3.5 ± 0.5	−7.2 ± 1.1

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(6) J. C. Southard and C. H. Shomate, *ibid.*, **64**, 1770 (1942).

(7) G. L. Humphrey and E. G. King, *ibid.*, **74**, 2041 (1952).

(8) F. R. Bichowsky and F. D. Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936, p. 90.

(9) National Bureau of Standards Selected Values of Chemical Thermodynamic Properties, Ser. I, Tables 8a (Mar. 31, 1948) and 10-3 (Mar. 31, 1947).

(10) L. S. Darken and R. W. Gurry, THIS JOURNAL, **67**, 1398 (1945).

(11) J. P. Coughlin, E. G. King and K. R. Bonnickson, *ibid.*, **73**, 3891 (1951).

(12) K. K. Kelley, U. S. Bureau of Mines Bull. 476 (1949), pp. 85 and 131.

Related Thermal Data.—Table III lists the heats, entropies and free energies of formation at 298.16° K. of the two silicates from the elements and from the oxides. The entropy values are derived from the compilation of Kelley[13] and the work of Humphrey, King and Kelley,[14] and Todd and Bonnickson.[15]

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(13) K. K. Kelley, U. S. Bureau of Mines Bull. 477 (1950).

(14) G. L. Humphrey, E. G. King and K. K. Kelley, U. S. Bureau of Mines, Report of Investigations 4870 (June, 1952).

(15) S. S. Todd and K. R. Bonnickson, THIS JOURNAL, **73**, 3894 (1951).

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NOTES

The Effect of Sodium Oxide on the Chromium Oxide Catalyzed Conversion of Aldehydes to Ketones[1]

BY J. R. COLEY[2] AND V. I. KOMAREWSKY

RECEIVED MARCH 1, 1952

In the course of a study[3] of the action of metallic oxide catalysts on alcohols, it was found that alcohols and aldehydes of "n" carbon atoms undergo a complex dehydrogenation–condensation reaction when passed over a chromia catalyst at 400° to form ketones of "$2n - 1$" carbon atoms. It was noted that a sodium hydroxide precipitated catalyst was quite active in contrast to a comparatively inactive ammonia precipitated catalyst.

It has therefore been of interest to determine the effect of sodium content in a chromia catalyst upon this reaction.

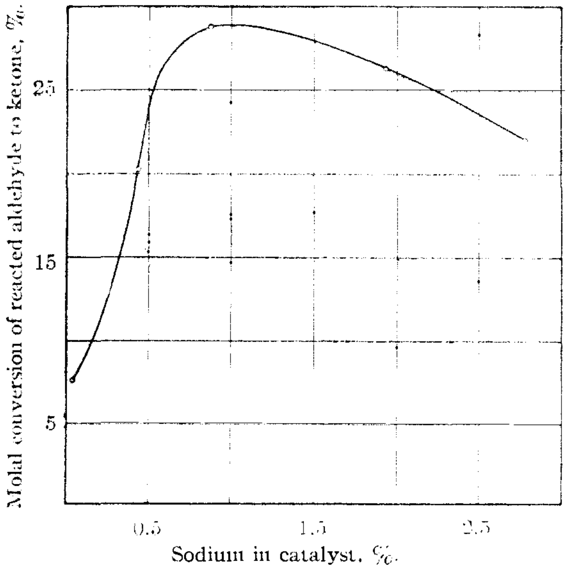

Fig. 1.—The effect of sodium oxide on the conversion of n-butyraldehyde to di-n-propyl ketone.

Experimental Part

Procedure.—The catalysts were prepared by redissolving a cold slurry of chromium hydroxide precipitate in cold excess sodium hydroxide. The chromite solution on standing overnight formed a chromium hydroxide gel. The gel was washed anion free, dried at 110°, screened to 8 mesh and heated in an atmosphere of hydrogen at gradually increased temperatures up to 500°. To vary the sodium content, portions of the catalyst, after washing but prior to drying, were agitated in sodium carbonate solutions of varying concentrations, filtered and dried. The method of sodium analysis was a modification of the triple acetate procedure devised by Kahane.[4]

The catalytic reaction procedure consisted of passing a three to one mixture of nitrogen and vaporized n-butyraldehyde over a granular (8–10 mesh) catalyst bed (volume 50 cc.), maintained at a temperature of 400° by an electrically heated furnace. A constant liquid space velocity of 0.1 was used for all runs. All products were distilled in a 20-inch super-cal Heli Grid Podbielniak Column.

Discussion of Results

The results obtained are given in Table I and Fig. 1.

TABLE I

DATA ON SODIUM CONTENT OF CHROMIA CATALYSTS *versus* YIELD OF KETONE

Weight % sodium	Molal conversion of reacted aldehyde to ketone,[a] %
0.04	7.6
.45	20.3
.88	28.8
1.93	26.3
2.79	22.1

[a] Dipropyl ketone, b.p. 144.18°.

These results indicate that the sodium content of a chromia catalyst has a definite effect on the catalytic activity for the dehydrogenation–condensation reaction discussed. This is consistent with the aldol mechanism proposed[3] for this ketone synthesis. The optimum sodium content was found to be approximately 1.0%.

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(1) From the Senior Problems of B. M. Joseph and S. C. Mikszta.

(2) Research Dept., Standard Oil Co. (Indiana), Whiting, Indiana.

(3) V. I. Komarewsky and J. R. Coley, THIS JOURNAL, **63**, 700 3269 (1941).

(4) E. Kahane, *Bull. soc. chim.*, **47**, 382 (1930).

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Preparation and Some Reactions of Indenyllithium

BY NORMAN H. CROMWELL AND DAVID B. CAPPS

RECEIVED MARCH 24, 1952

In connection with a general project in this Laboratory concerned with the synthesis and reactions of cyclic ketones, methods of preparing β-(1-in-